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Adsorption and preconcentration of divalent metal ions in fossil fuels and biofuels: Gasoline, diesel, biodiesel, diesel-like and ethanol by using chitosan microspheres and thermodynamic approach

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ABSTRACT

Biodiesel and diesel-like have been obtained from soybean oil by transesterification and thermal cracking process, respectively. These biofuels were characterized as according to ANP standards by using specific ASTM methods. Ethanol, gasoline, and diesel were purchased from a gas station. Deacetylation degree of chitosan was determined by three distinct methods (conductimetry, FTIR and NMR), and the average degree was 78.95%. The chitosan microspheres were prepared from chitosan by split-coating and these spheres were crosslinked using glutaraldehyde. The surface area of microspheres was determined by BET method, and the surface area of crosslinked microspheres was 9.2 $m^2\,g^{-1}$. The adsorption isotherms of cooper, nickel and zinc on microspheres of chitosan were determined in petroleum derivatives (gasoline and diesel oil), as well as in biofuels (alcohol, biodiesel and diesel-like). The adsorption order in all fuels was: Cu > Ni > Zn. The elution tests presented the following preconcentration degrees: >4.5 to ethanol, >4.4 to gasoline, >4.0 to diesel, >3.8 to biodiesel and >3.6 to diesel-like. The application of chitosan microspheres in the metal ions preconcentration showed the potential of this biopolymer to enrich fuel sample in order to be analyzed by flame atomic absorption spectrometry.

1. Introduction

Fuel is a material used for burning as a source of heat or power. The main fossil fuels used in automotives are gasoline and diesel and the most important biofuels used in vehicles are ethanol biodiesel and diesel-like [1]. Nowadays, fuel industries have many challenges to be reached such as: replacing the fossil fuels with biofuels in other to decrease SO, NO, CO emissions, as well as, reducing global warming problems [2,3]. Other problem is the presence of metal ions in fuels, which can induce corrosion in the vehicle components [4–10], and increase the formation of gums during fuel burning [11]. These gums can be deposited in filters and distribution lines and their accumulation can cause engine wear and have adverse effects on engine performance, efficiency, and durability [4,5,11]. Thus, it is essential to develop methods to determine traces of metals in fuels used in automotives. However, the direct determination of metal ions at trace levels in fuels by ET AAS is not simple and the analysis can be unreliable. The direct determination in ethanol needs more expensive apparatus such as electrothermal atomic absorption spectrometry (ET AAS), inductively coupled plasma atomic emission spectroscopy (ICP AES) or inductively coupled plasma mass spectrometry (ICP-MS) [4,6,7] and for determination of metals in gasoline, diesel, biodiesel and diesel-like, the analysis needs ET AAS, ICP-AES or ICP-MS apparatus and organometallic standards, which increase the costs to quantify these trace metals. In order to solve these problems, methods using liquid–liquid extraction, ion exchange and preconcentration procedures have been used [1,4,9]. Among them, preconcentration/elution is a simple method, which has presented interesting results [8,12,13]. On the other hand, this methodology is extensively used to aqueous samples and ethanol fuel, whereas it is a little applied in gasoline and diesel analysis. It is important to highlight that there are not any reported data about the application of preconcentration to quantify metal ions in biodiesel and diesel-like. Then, the development of a methodology to determine metal ions by using preconcentration in distinct fuel matrixes (ethanol, gasoline, diesel, biodiesel, and diesel-like) is a gap in the scientific literature. Many supports have been applied to preconcentrate metal ions: such as zeolites, mixed oxides, coals, clays, sawdust, polymers, exchange resins, modified silicas, nanoporous silicas, and

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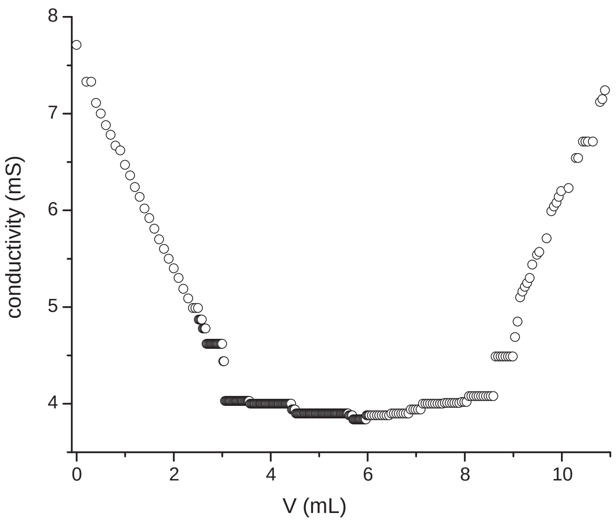

Fig. 1. Conductimetric titration curve of chitosan with NaOH.

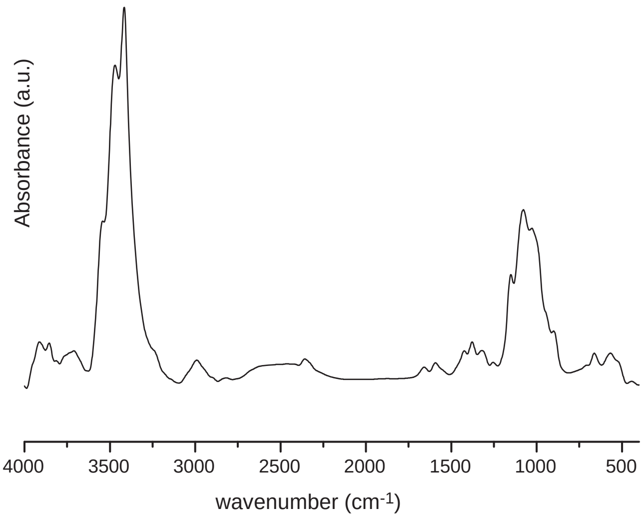

Fig. 2. FTIR spectrum of chitosan.

chitosan [14–18]. Among these materials, chitosan must be highlighted because it is a low-cost material, which can be obtained from fishery wastes (crab and prawn). Besides, the application of these wastes can bring benefits to poor Brazilian fishermen breadwinners [14,19].

Thus, the present study is focused on copper, nickel and zinc adsorption and preconcentration on chitosan microspheres in ethanol, gasoline, diesel, biodiesel and diesel-like media and the thermodynamic data for these interactions.

2. Experimental

2.1. Chemicals

Vegetable oil (Soya), gasoline and diesel (ANP), NaOH (Vetec), methanol (Sigma), H_3PO_4 (Vetec), $MgSO_4$ (Vetec) were used without any purification.

2.2. Transesterification and biodiesel characterization

Transesterification reactions were followed by using 10.0 g of buriti oil, 1.5 g of methanol and 0.1 g of NaOH. Potassium hydroxide was completely dissolved in MeOH under stirring in a glass batch reactor equipped with a mechanical stirrer. Then, the vegetable oil was added into the mixture and maintained under stirring for 2 h at 50 °C. The resulting product was washed with a saturated aqueous NaCl solution. The organic phase was separated by decantation and dried with anhydrous $MgSO_4$. Recovered esters were analyzed by HPLC, using a method published elsewhere [20,21], in a Shimadzu CTO-20A chromatograph with UV–VIS detector at $\lambda = 205$ nm, equipped with Shim-Pack VP-ODS column (C-18, 250 mm, 4.6 mm i.d.).

2.3. Pyrolysis and diesel-like characterization

Pyrolysis experiments were carried out at temperatures ranging from 350 to 400 °C in a 5 L stainless steel batch unit, as described in detail before [22]. The vegetable oil (2 L) was introduced into the pyrolysis reactor and then heated by an external electric resistance. The temperature was measured at two sites with calibrated thermocouples. When the temperature inside the reactor achieved 350 °C, the vegetable oil was pyrolyzed, vaporized and a vapor feed left the reaction, by the upper side at temperatures ranging from 200 to 250 °C. Then, the vaporous feed entered into a water cooled heat exchanger. Two liquid fractions were obtained in the collector: an aqueous fraction and an organic fraction. These fractions were separated by decantation and the organic phase was distilled according to standard oil laboratory techniques. The distillates were separated into four fractions with the following distillation temperature ranges: (a) $T < 80$ °C; (b) 80 °C $\leq T < 140$ °C; (c) 140 °C $\leq T < 200$ °C; (d) 200 °C $\leq T$ (heavy fraction). The different fractions were weighed and the heaviest one was analyzed according to ASTM D86 standard methods for petroleum fuels [23].

Diesel-like was characterized by acidity index, density, kinematic viscosity, cetan index, copper corrosion, carbon residue and fulgor point [24–29].

2.4. Chitosan characterization

Deacetylation degree of chitosan was determined by three distinct methods: conductimetric titration, FTIR spectroscopy and ^{1}H-NMR spectrometry.

The conductimetric titration was carried out with 200 mg of chitosan suspended in 50 mL of water and 0.1 mL of HCl. After fully dissolution of the biopolymer, this solution was titrated by standardized NaOH 0.17 mol L^{-1}. Titration was monitored by a conductimetry Adamo MCA 150.

Infrared spectrum of solid sample in the 4000–400 cm^{-1} range were performed in KBr pellets, with a resolution of 4 cm^{-1}, by accumulating 60 scans on a Jasco 4100 spectrophotometer.

NMR ^{1}H was obtained on a Varian Mercury Plus 7.05 T, 300 MHz to ^{1}H. This analysis was carried out with disbanded chitosan in D_2O/HCl (100:1, v/v) at room temperature.

The chitosan microspheres images were morphologically observed in an Optical Video-microscope Bell Optics.

The chitosan and chitosan microspheres surface areas were determined through isotherm adsorption–desorption, employing a Quantachrome Nova 2200 analyzer. It was performed by a preliminary drying at 100 °C under reduced pressure for 12 h.

The presence of residual metal ions in chitosan samples were determined by using 0.25 g of chitosan dissolved in 5 mL of HNO_3. These samples were digested in a microwave Milestone Model Ethos D with 250 W by 20 min. Digested volumes were completed to 10 mL with water and the elements Ni, Zn and Cu were analyzed in ICP-AES Varian Liberty II.

2.5. Preparation of chitosan microspheres

The chitosan microspheres were prepared according to the method proposed by Rorrer et al. (split-coating) [30], with some modifications from Prado et al. [31], as represented in Fig. 2. Chitosan 10% (w/v) was dissolved in 5% (v/v) acetic acid at room temperature. The solution was homogenized for 2 h and after dripped in a coagulant solution of sodium hydroxide 10% (w/v) kept under stirring. Then, the microspheres were washed with deionized water until reaching pH 7.0. Once neutralized, the gelled beads were crosslinked in a 25% glutaraldehyde solution, without stirring for 2 h. After that, microspheres were filtered, washed with deionized water and then with acetone and dried [31].

2.6. Divalent metal ions adsorption

The adsorption process was followed batchwise in ethanol, gasoline, diesel, biodiesel and diesel-like solutions for the divalent cations copper, nickel and zinc at 25 °C. A series of samples of 250 mg of chitosan microspheres was suspended in 50.0 mL of metal chloride solutions of different concentrations, varying from zero to 5 mmol L^{-1}, in presence of 0.5 mL of Triton X-100 10% in order to allow the solubilization of the metal ion in fuel samples, for this, the samples were homogenized during 20 min.

The suspension was mechanically stirred for 12 h in all solutions. The amount of cation in the supernatant was determined by using a FAAS Varian 220 spectrometer and, consequently, the amount adsorbed was determined by difference. All samples were analyzed in triplicate.

2.7. Calorimetric analyses

The thermodynamic parameters of the interaction between the metal ion and chitosan microspheres were followed by calorimetric titration in an adiabatic calorimeter PAR 6755. In this experiment, 500 mg of the microspheres were suspended in 100 mL of ethanol, gasoline, diesel, biodiesel and diesel-like solutions, equilibrated at 25 °C (thermostatically controlled), and titrated 0.05 g L^{-1} cation solution of each cation with 0.1 (v/v) Triton X-100 10%.

2.8. Preconcentration studies

The preconcentration studies were followed in a distinct 25 mL solution of 0.2 mg L^{-1} of Cu, Ni and Zn for all fuel samples. 0.1 g of chitosan microspheres were suspended in 25 mL of these samples, which was stirred during 30 min in an automatic tube stirrer Quimis Q220A. Chitosan microspheres were separated from solution by centrifugation and HCl was added in different concentrations 0.10, 0.25, 0.50, 1.0 and 1.5 mol L^{-1} in order to elute the metal ion adsorbed in chitosan microspheres. The elution occurred during 30 min. The eluted solutions were separated by centrifugation. Acid aqueous solution was analyzed in an AAS spectrometer Varian 220. All analyses were performed in triplicate.

In order to confirm the original results, 0.2 mg L^{-1} of each metal in each fuel sample was analyzed in an ICP-AES Varian Liberty II Radial.

To quantify the metal ions in ethanol fuel, it was applied the methodology used by Brüning and Malm [32], which consists in the evaporation of the ethanol sample at 70 °C up to dark color, followed by solubilization of 1.0 mL of nitric acid and metal analysis. To determine the amount of metal ions in gasoline, diesel, biodiesel and diesel-like, it was applied the methodology used by Santelli et al. [33], which is based on solubilization of the 1.0 mL of sample in 0.5 mL of HNO_3 and 0.5 mL of Triton X-100 10% (v/v), and this emulsion is analyzed.

3. Results

3.1. Biodiesel and diesel-like characterization

The result of transesterification of soybean oil with methanol was observed in a HPLC, which showed that the final product presented 96% of biodiesel biodiesel, 1% of triglycerides and 3% of identified compounds; diglycerides, monoglycerides and fatty acids were not detected.

All parameters analyzed acidity index, density, kinematic viscosity, cetan index, copper corrosion, carbon residue and fulgor point were performed according to Brazilian legislation, as reported in detail before.

3.2. Chitosan characterization

Conductimetric titration is shown in Fig. 1. This figure presents 3 distinct stages: the first one (between 0.0 and 3.0 of added titrant) corresponds to neutralization of the excess of hydrochloride acid; the second stage (between 3.0 and 8.6 mL of added titrant) is related to neutralization of protonated amine groups of chitosan; the last stage is related to conductivity of the increase of the OH^- ions released in solution from titrant.

The deacetylation degree (DD) of chitosan was obtained by applying Eq. (1), using $m = 0.1988$ g (chitosan mass used), $C = 0.171$ mol L^{-1} (standardized concentration of NaOH) and the difference between the second and the first inflection points of conductivity curve. Thus, the DD obtained was 77.55%.

$$\mathrm{DD} = \frac{16.1 \times C(V_2 - V_1)}{m} \qquad (1)$$

FTIR spectrum of chitosan is presented in Fig. 2. Many characteristic bands can be observed in this spectrum such as: a broad large band between 3600 and 3100 cm^{-1} related to O–H and N–H_2 stretchings of chitosan; two peaks, one at 2950 and other at 2870 cm^{-1} assigned to C–H stretching of sp^3 carbon. A peak at 1655 cm^{-1} related to C=O from amide groups, a peak at 1590 cm^{-1} asigned to out plane deformation of –NH_2, peaks at 1421 and a peak at 1340 cm^{-1} related to glycosaminic ring. The peaks between 1200 and 900 cm^{-1} are assigned to C–O stretching of glycosaminic ring [34,35].

Deacetylation degree was calculated from infrared spectrum as well as, by two different equations, Eqs. (2) and (3).

The infrared absorption intensities were inserted in these equations and DD values gave 79.4 and 80.01% by applying Eqs. (2) and (3), respectively.

$$\mathrm{DD} = 100 - \left(\frac{A_{1655}/A_{3450}}{1.33} \times 100\right) \qquad (2)$$

$$\mathrm{DD} = 100 - \left[\frac{(A_{1320}/A_{1420}) - 0.3822}{0.03133}\right] \qquad (3)$$

NMR spectrum in Fig. 3 presented a singlet at 2 mg L^{-1} related to methyl group of acetoamide group, a triplet between 2.85 and 2.95 mg L^{-1} assigned to hydrogen of the carbon 3 of glycosamine ring, a singlet at 3.17 mg L^{-1} related to hydrogens 5 and 6 and a duplet between 3.4 and 4.1 mg L^{-1} assigned to hydrogens of the ring. The degree of deacetylation of the chitosan was calculated using Eq. (4) from data obtained from NMR ^{1}H (Fig. 3).

$$\mathrm{DD} = 100 - \left(\frac{I_{\mathrm{met}}/3}{I_{\mathrm{H2-6}}/6} \times 100\right) \qquad (4)$$

where I_{met} is the integral intensity of the signal from the methyl protons of acetamide groups, $I_{\mathrm{H2-6}}$ is the sum of integral intensities of the signals from the H atoms bonded to carbons 2–6 of the glycosidic ring, in the region between 1 and 4 mg L^{-1} and DD is the degree

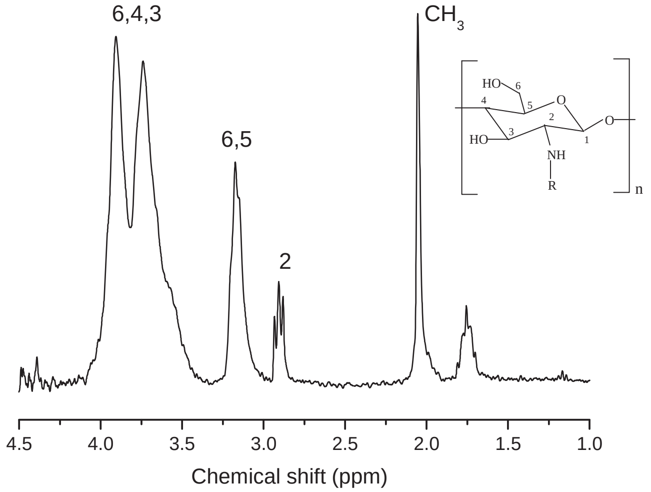

Fig. 3. ^{1}H-NMR spectrum of chitosan.

of deacetylation [35–37]. From the application of the obtained data on Eq. (3), the DD was determined to be 79.2%.

The DD obtained values for chitosan by distinct techniques presented very similar values in a medium value of DD = 79.2 ± 1.77.

Pre-existing metal ions in chitosan were determined due to it is very important to analyze the amount of residual metal ions in chitosan in order to avoid any induction of the results. The amount of Cu, Ni and Zn found per gram of chitosan was 0.386, 0.405 and 0.543 μg, respectively.

The surface area values of these materials were calculated by applying the BET equation in N_2 isotherms (Fig. 4), which gave 4.2; 14.1 and 9.6 $m^2\,g^{-1}$ for start chitosan, chitosan microspheres and crosslinked chitosan microspheres, respectively. This fact evidences that the formation of microspheres from start chitosan causes a significant increase on the surface area of the material due to a morphological organization of the material, which is one of the new adsorbent qualities of this material when compared with the start material. On the other hand, the reticulation causes the decrease of the surface area because of the introduction of glutaraldehyde frameworks between linear polymeric chains of chitosan, which reduces the surface area after incorporation of organic groups, as shown in Fig. 4. This fact can be easily explained due to these groups block partially the adsorption of nitrogen molecules on the surface, resulting in a decrease of the surface area.

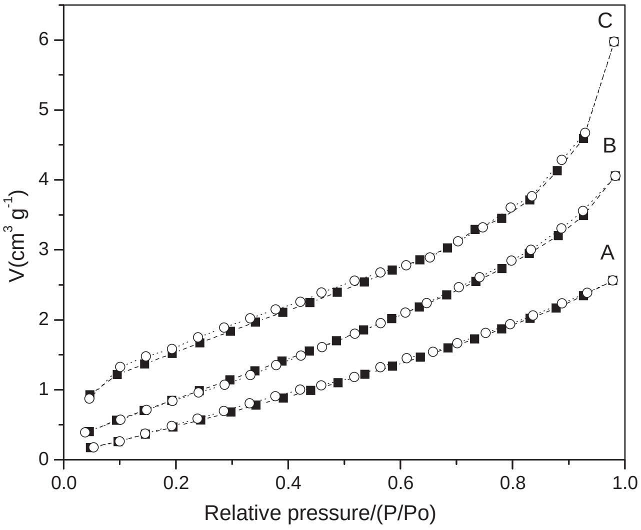

Fig. 4. Nitrogen adsorption–desorption isotherms for the samples: chitosan (A), crosslinked chitosan microspheres (B) and chitosan microspheres (C).

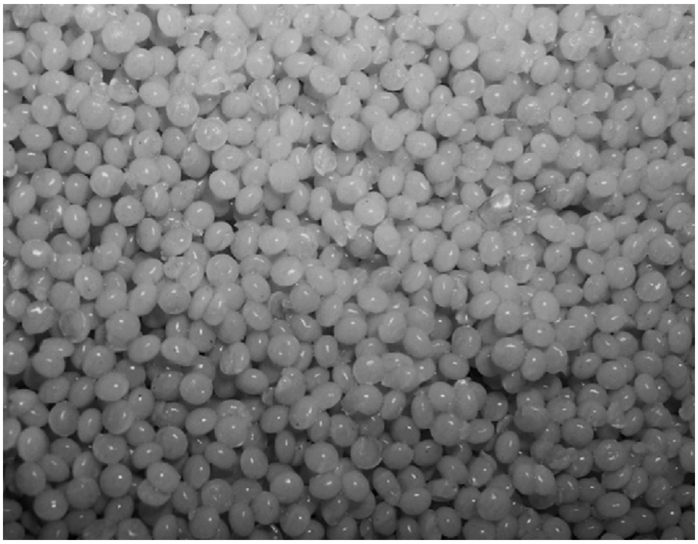

Fig. 5. Crosslinked chitosan microspheres image.

Optical image of microspheres showed that these spheres presented a homogeneous spherical morphology with a medium diameter less than 500 μm, as illustrated in Fig. 5.

3.3. *Adsorption studies*

The chitosan microspheres were applied to adsorb Cu, Zn and Ni from ethanol, gasoline, diesel, biodiesel and diesel-like. The adsorption capacity of chitosan microspheres was evaluated by measuring the sorption isotherms.

The number of moles of metals adsorbed per gram of adsorbent (N_f; mol g^{-1}) was obtained from Eq. (5) [7,13].

$$N_f = \frac{n_i - n_s}{m} \tag{5}$$

where n_i is the initial number of moles of divalent metal ions added to the system, n_s is the number of moles at equilibrium after adsorption, and m is the mass (g) of chitosan. The adsorptive behavior represented by the number of moles adsorbed (N_f), versus the number of moles at equilibrium per volume of solution (C_s) is presented in Fig. 5A.

The experimental data were applied into the general equation of the modified Langmuir model presented in Eq. (6) [7,13].

$$\frac{C_S}{N_f} = \frac{1}{N_S K} + \frac{C_S}{N_S} \tag{6}$$

where C_s is the concentration (mol dm^{-3}) of the solution at equilibrium, N_s is the maximum amount of divalent metal ion adsorbed per gram of chitosan microsphere (mol g^{-1}), which depends on the number of adsorption sites, and K is a equilibrium constant (mol L^{-1}).

Figs. 6–10 show the divalent metal ions adsorption isotherm curves in ethanol, gasoline, diesel, biodiesel and diesel-like, respectively. The values of the maximum amount of Cu, Zn and Ni in each fuel are listed in Table 1.

Adsorption isotherms for all fuels presented a similar behavior and in all cases the adsorption capacity of chitosan showed the following sequence: Zn < Ni < Cu. More details about adsorption behavior can be observed in Table 1.

Table 1 shows that the maximum adsorption capacity per fuel followed the sequence: ethanol < diesel-

Table 1
Maximum adsorption capacity of chitosan microspheres for Cu, Zn and Ni, per studied fuel.

	Ethanol	Gasoline	Diesel	Biodiesel	Diesel-like
Copper					
mmol g^{-1}	0.71 ± 0.02	1.18 ± 0.12	1.19 ± 0.04	1.38 ± 0.02	1.00 ± 0.02
mg g^{-1}	45.12 ± 1.10	74.98 ± 7.50	75.61 ± 2.34	87.69 ± 1.49	63.54 ± 1.14
Nickel					
mmol g^{-1}	0.68 ± 0.01	1.09 ± 0.09	1.18 ± 0.01	1.31 ± 0.08	0.96 ± 0.03
mg g^{-1}	39.91 ± 0.55	63.97 ± 5.37	69.25 ± 0.90	76.88 ± 4.46	56.34 ± 1.86
Zinc					
mmol g^{-1}	0.58 ± 0.01	1.02 ± 0.05	1.09 ± 0.06	1.26 ± 0.07	0.93 ± 0.04
mg g^{-1}	37.92 ± 0.49	66.70 ± 3.07	71.28 ± 3.78	82.39 ± 4.86	60.81 ± 2.49

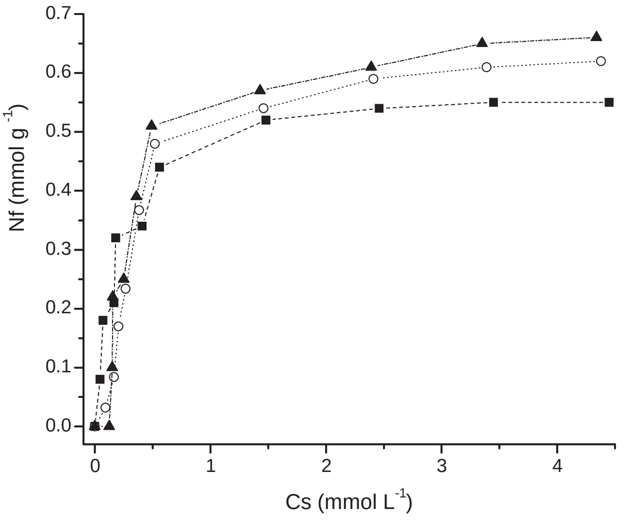

Fig. 6. Adsorption isotherms of Cu (▲), Ni (○) and Zn (■) on chitosan microspheres in ethanol.

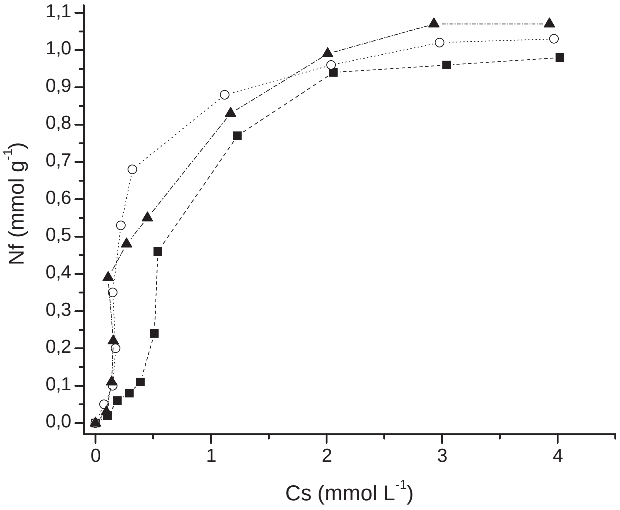

Fig. 8. Adsorption isotherms of Cu (▲), Ni (○) and Zn (■) on chitosan microspheres in diesel.

like < gasoline < diesel < biodiesel. This figure shows that copper was the best adsorbed and zinc was the worst in all five fuels.

3.4. Preconcentration studies

In the preconcentration studies, the mass of chitosan microspheres per time of adsorption (elution time), was constant and the unique variable was the concentration of HCl.

The obtained results of the elution of the metal ion with different concentration of HCl in ethanol, gasoline, diesel, biodiesel, and diesel-like is shown in Table 2. Data showed that in a low concentration of HCl (0.1 and 0.2 mol L^{-1}), the elution was not efficient for these metal ions. On the other hand, in a concentration above 0.5 mol L^{-1} of HCl, the recovery of the metal ions was efficient, presenting enrichment factors in ethanol fuel of 4.56; 4.75; 4.78 times for Zn, Ni, and Cu, respectively.

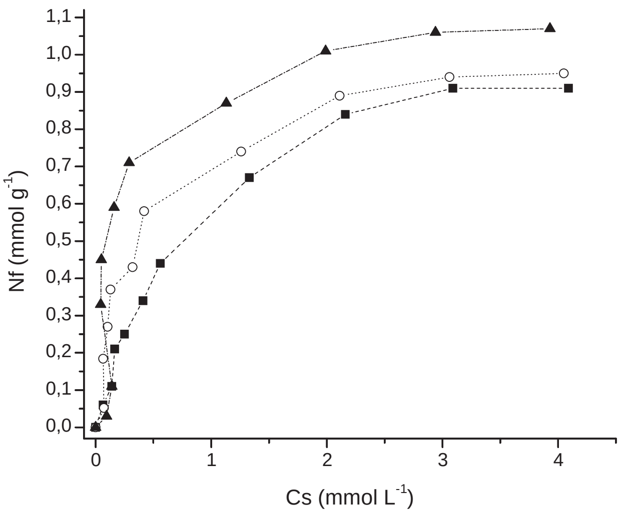

Fig. 7. Adsorption isotherms of Cu (▲), Ni (○) and Zn (■) on chitosan microspheres in gasoline.

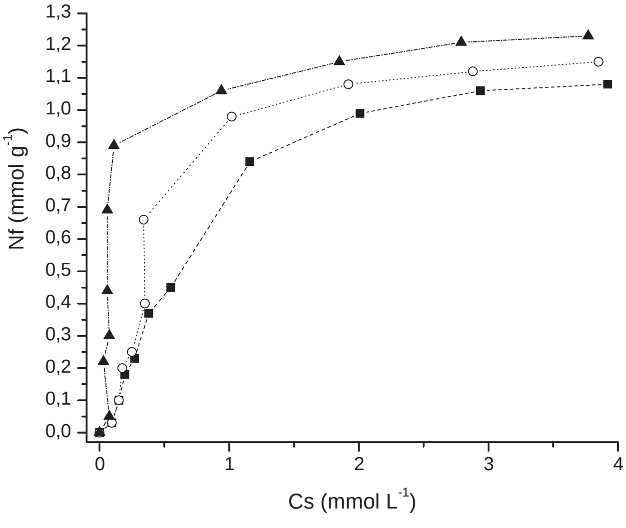

Fig. 9. Adsorption isotherms of Cu (▲), Ni (○) and Zn (■) on chitosan microspheres in biodiesel.

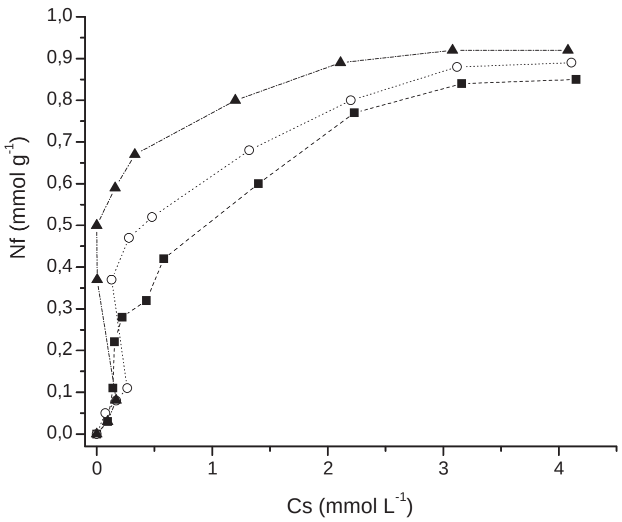

Fig. 10. Adsorption isotherms of Cu (▲), Ni (○) and Zn (■) on chitosan microspheres in diesel-like.

The preconcentration studies of Cu, Zn and Ni in gasoline, presented a good elution above HCl 0.20 mol L^{-1} for Cu and above 0.50 mol L^{-1} for Zn and Ni. The application of chitosan microspheres in metal ions preconcentration resulted in enrichment factors of 4.42, 4.64, and 4.45 times for Cu, Ni and Zn, respectively.

In the preconcentration studies of Cu, Zn and Ni in diesel, the preconcentration factor increased up to HCl 1.0 mol L^{-1} maintaining constant above these values. The enrichment factors for diesel were 4.04, 4.47 and 4.36 times for Cu, Ni and Zn, respectively.

Despite the ethanol and gasoline elution data, the elution curves of diesel reached the maximum enrichment fact only at HCl 1.0 mol L^{-1} whereas in ethanol and in gasoline the maximum preconcentration factor was reached at HCl 0.5 mol L^{-1}. In diesel case, the elution assays with HCl 0.5 mol L^{-1} were less effective. These results can be explained due to diesel presented a viscosity higher than gasoline and ethanol. Thus, amount of diesel can be adsorbed on chitosan surface, forming a protecting shield which blocks the access of acid in quelant sites of chitosan.

In the preconcentration studies of Cu, Zn and Ni in biodiesel, a preconcentration behavior similar to diesel was presented and the enrichment factors were 3.87; 3.82 and 4.03 for Cu, Ni and Zn, respectively. The enrichment factors lower than those of diesel can be explained by the presence of esters groups in biodiesel structure, which can interact with metal ions decreasing the interaction with chitosan.

The preconcentration studies of Cu, Zn and Ni in biodiesel, presented similar preconcentration results at any concentration of HCl, with enrichment factors of 3.74; 3.71 and 3.59 times for Cu, Ni, and Zn, respectively. This phenomenon can be explained by the low solubility of the metal ions in diesel-like, with facilitates the partition of the metals at low concentrations of HCl. However, the enrichment factor was lower than others and this fact can be occurred due to the presence of carboxylic acids and other oxygenated compounds capable to interact with metal ions making the interaction with chitosan difficult.

3.5. *Application of the methodology in commercial samples*

Commercial samples of diesel, gasoline, and ethanol were obtained from Gas Station and biodiesel and diesel-like were synthesized in laboratory. Metal ions were analyzed by a preconcentration method with chitosan microspheres by using a FAAS Varian AA2200 and in order to compare the obtained results, the fuels were analyzed according to Brüning and Malm [32] methodology for ethanol and Santelli et al. [33] methodology for diesel, gasoline, biodiesel and diesel-like using an ICP-AES Varian Liberty II Radial.

Table 2
Quantification of Cu, Zn and Ni in commercial fuels by analyzed in ICP-AES and by applying preconcentration system and analyzed by FAAS.

	Ethanol	Gasoline	Diesel	Biodiesel	Diesel-like
Cu					
FAAS	4.83 ± 0.21	0.89 ± 0.34	0.32 ± 0.22	N.D.	N.D.
D.L.	0.0084	0.0091	0.01	0.0104	0.0108
ICP-AES	5.22 ± 0.15	0.81 ± 0.08	0.28 ± 0.17	N.D.	N.D.[a]
D.L.	0.011361	0.011737	0.012105	0.011622	0.011076
Ni					
FAAS	N.D.	0.09 ± 0.11	N.D	N.D.	N.D.
D.L.	0.0849	0.0087	0.009	0.0106	0.0109
ICP AES	N.D.	N.D.	N.D.	N.D.	N.D.
D.L.	0.0059247	0.006525	0.006356	0.006183	0.006483
Zn					
FAAS	3.76 ± 0.42	1.14 ± 0.39	0.35 ± 0.39	N.D.	N.D.
D.L.	0.0088	0.0091	0.0092	0.01	0.0112
ICP AES	3.58 ± 0.33	1.02 ± 0.08	0.45 ± 0.12	N.D.	N.D.
D.L.	0.016565	0.015045	0.016689	0.016114	0.016296

[a] D.L.: detectable limits; N.D.: not detectable.

All results were listed in Table 2. The obtained results for samples showed that the methods presented a concordance up to 92.58%. Any metal ions were not detected in biodiesel and diesel-like in both methodologies. These results were expected due to these fuels were synthesized in laboratory, being free from metallic parts. The advantage of the application of chitosan microspheres in the determination of metal ions in fossil fuels and in biofuels is that this application allows the quantification of metal ions using a technique (ET AAS) cheaper and easier than traditional methods (ICP-AES or ICP-MS). It must be highlighted that there are many papers about preconcentration of metal ions in water in ethanol fuel. However, there are very few papers about preconcentration of metal ions in diesel and gasoline and mainly in biodiesel and diesel-like.

3.6. *Thermodynamic studies*

In order to clarify all gaps in the interaction between chitosan microspheres and metal ions present in fossil fuel or in biofuels, calorimetric studies were carried out.

Separated titration experiments were carried out in order to determine the component parts, named: (a) the heat evolved by the chitosan–M^{2+} interaction (Q_{tit}), (b) the heat of solvation of the chitosan (Q_{sol}), and (c) the heat of dilution of M^{2+} solution (Q_{dil}). The net heat change Q_{tot} (d) is given by Eq. (7) [18,19,38].

$$\Sigma Q_{\text{tot}} = \Sigma Q_{\text{tit}} + \Delta Q_{\text{sol}} - \Delta Q_{\text{dil}} \qquad (7)$$

Since the heat of solvation of the aqueous suspended modified material was null, the expression was reduced to Eq. (8) [18,19,38].

$$\Sigma Q_{\text{tot}} = \Sigma Q_{\text{tit}} - \Delta Q_{\text{dil}} \qquad (8)$$

The enthalpy of interaction, $\Delta_R H\,(Q_{\text{tot}}/m)$, was obtained from an expression to the modified Langmuir equation represented in Eq. (9) [18,19,38].

$$\frac{\Sigma X}{\Sigma \Delta_R H} = \frac{1}{(K-1)\Delta_{\text{mono}} H} + \frac{\Sigma X}{\Delta_{\text{mono}} H} \qquad (9)$$

where ΣX is the sum of the molar fractions of the divalent metal ions remaining in solution after adsorption and $\Sigma \Delta_R H$ is the enthalpy of interaction per gram of chitosan microspheres.

Table 3
Thermodynamic data (ΔH, ΔG and ΔS) of chitosan microspheres for Cu, Zn and Ni, per studied fuel.

	$-\Delta H$ (kJ/mol)	$-\Delta G$ (kJ/mol)	ΔS (J/mol K)
Ethanol			
Cu	44.1	24.2±	−66
Ni	32.4	22.1±	−34
Zn	31.1	20.1±	−36
Gasoline			
Cu	48.1	41.4±	−22
Ni	33.7	38.4±	16
Zn	32.2	34.2±	7
Diesel			
Cu	45.2	40.2±	−17
Ni	33.1	39.4±	21
Zn	31.7	37.7±	20
Biodiesel			
Cu	22.1	45.0±	77
Ni	16.4	42.8±	89
Zn	16.2	41.1±	84
Diesel-like			
Cu	21.8	36.7±	50
Ni	17.1	34.6±	59
Zn	15.9	33.6±	59

ΔH, of the interaction process was calculated from $\Delta_{\mathrm{mono}}H$ and the maximum number of moles inserted, N_s, using Eq. (10).

$$\Delta H = \frac{\Delta_{\mathrm{mono}}H}{Ns} \tag{10}$$

The Gibbs free energy changes may be calculated from Eq. (11),

$$\Delta G = -RT \ln K \tag{11}$$

and the entropy ΔS was determined by Eq. (12).

$$\Delta S = \frac{\Delta H - \Delta G}{T} \tag{12}$$

All thermodynamic data of the adsorption of Cu, Zn, and Ni by chitosan microspheres in ethanol, gasoline, diesel, biodiesel and diesel-like are listed in Table 3. These results show that all interactions between the metal ion and chitosan microspheres are spontaneous and enthalpically favored (exothermic) for all fuel samples. ΔG data show that the adsorption on chitosan microspheres followed the sequence: ethanol < diesel-like < gasoline < diesel < biodiesel for any metal ions. Moreover, the ΔH data were interesting once ΔH values for biodiesel and diesel-like were much lower than other fuels. This fact occurred because of the high obtained values of heat of dilution of the metal ion on fuel (Q_{dil}), confirming the interaction between the metal ions with (which is Lewis acid) biodiesel and diesel-like, which must be occurred due to oxygenated Lewis basic centers present in biodiesel and diesel-like with metal ions (which is Lewis acid). The thermodynamic data corroborate with eluting behavior. Other interesting aspect is the ΔH of Cu–chitosan microspheres is much higher than other interactions in all fuels, as reported before [39], which suggested the high affinity of amine basic groups of chitosan for copper.

4. Conclusion

This paper showed the first work that reports the metal ions preconcentration in fossil fuels (diesel and gasoline) and biofuels (ethanol, biodiesel and diesel-like) in the literature. All results showed that the chitosan microspheres were obtained with success and they were able to adsorb and preconcentrate copper, zinc and nickel from ethanol, gasoline, diesel, biodiesel, and diesel-like. The adsorption followed the sequence zinc < nickel < copper in all fuels. Chitosan microspheres interacted with metal ions in the following sequence: ethanol < diesel-like < gasoline < diesel < biodiesel. Thermodynamic data show that interactions with all metal ions with chitosan microspheres were spontaneous ($\Delta G < 0$) and enthalpically favored (exothermic). Elution data and thermodynamic studies suggest that the metal ions interact with biodiesel and diesel-like by oxygenated groups present in these fuels competing with chitosan microspheres during preconcentration processes.

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